1. Introduction

The flue gas from oxy-coal combustion typically contains 1,000 to 10,000 ppm SO\textsubscript{x} and 100 to 1,000 ppm NO\textsubscript{x}. During combustion, SO\textsubscript{2} and NO are the thermodynamically favoured species. At ambient temperature conditions, the equilibrium changes towards SO\textsubscript{3} and NO\textsubscript{2} although for atmospheric pressure conditions, the reactions are too slow for an extensive oxidation given the typical residence time in the flue gas train. In the oxy-fuel flue gas train the elevated pressure increases the gas concentrations (mol/m\textsuperscript{3}) and, thereby, the reaction rates are increased. The solubility of NO\textsubscript{2} is high, and the water that condensates during CO\textsubscript{2} compression will absorb NO\textsubscript{2}. In the liquid phase, NO\textsubscript{2} participates in a series of reactions, including both dissolved nitrogen and sulphur species. The initial experience from oxy-fuel combustion tests has shown that both nitric and sulphuric acid are formed in the flue-gas train, see for example White et al. (2008), Thébault et al. (2009), and Torrente-Muriciano et al. (2010). In connection to these observations, the so called “lead-chamber mechanism” is commonly discussed as an explanation to the formation of sulphuric acid. Yet, the lead-chamber mechanism requires highly concentrated sulphuric acid (70-80wt%), which is normally not present during the flue gas treatment process in large quantities. Therefore, this mechanism is not likely to be responsible for the extensive formation of acids observed, although it could be activated to some extent.

The understanding of SO\textsubscript{x} and NO\textsubscript{x} chemistry in the flue gas train is important to develop technical solutions for emission control, but also to predict conditions with high acid formation and for material issues. So far, the work performed on pressurized flue gas systems is limited to experimental observations, while this work aims to evaluate reaction kinetics relevant to NO\textsubscript{x} and SO\textsubscript{x} chemistry under conditions relevant to flue-gas compression.

2. Methodology

The model is described by Petersson et al. (2011) and only a brief summary is given here. The reaction mechanism is based on the work by Pires and Rossi (1997) to which subsets are added to describe the conditions in pressurized oxy-fuel flue gases. The system is described by a plug-flow reactor including gas and liquid phase reactions as well as mass transfer between phases. The mass transfer model is based on the two-film theory. The model is run under conditions representative for an oxy-fuel power plant. The flue gas introduced to the reactor is saturated with water and contains 3000 ppm SO\textsubscript{2}, 650 ppm NO\textsubscript{x} (NO:NO\textsubscript{2} = 10:1), and 5% oxygen. In the reference
case the pressure is 20 bar, temperature is 25°C, residence time is 100 seconds, and ratio between liquid and gas is 1/7000 m³/Nm³. This work discusses the reaction chemistry of the system and evaluates the influence of pressure, mass transfer, and liquid content.

3. Results

Figure 1 shows concentration profiles of NO₂, N₂O and the sum of nitrogen (total-N) in the gas phase (Figure 1a and b) and the main liquid species (c and d) calculated for the reference case at 5 and 20 bar respectively. At 5 bar, the absorption of NOₓ is low, which is shown by the total-N curve and the low concentrations of nitrogen in the liquid. This is a consequence of the strong pressure dependence of the NO oxidation, which governs the complete chemistry. Dissolved NO and NO₂ rapidly react with water and form HNO₂ and HNO₃. HNO₂ is unstable in the liquid phase and will dissociate to HNO₃ and NO. However, H₂SO₃, which forms from absorbed SO₂, is the dominating species in the liquid phase and will also react with HNO₂ through the Raschig mechanism (Raschig 1904). This mechanism is responsible for the production of H₂SO₄ and N₂O as observed in Figure 1. The reaction between H₂SO₃ and HNO₂ is generally faster than the dissociation of HNO₂. Thus, a flue gas containing NOₓ and SOₓ may form H₂SO₄ and N₂O. N₂O is not soluble in water and is released to the gas phase where it remains as a stable product. If NO₂ and HNO₂ are not present in the system, the formation of H₂SO₄ is drastically decreased. If instead SO₂ is removed from the system, NO and NO₂ may be absorbed depending on the NO oxidation reaction, and, the dissociation of HNO₂ will be completed with HNO₃ as the final product.

![Graph showing concentration profiles](image)

Figure 1. Gas (a and b) and liquid (c and d) phase concentration profiles at 5 bar (a and c) and 20 bar (b and d). Temperature is 25°C, and the ratio between liquid and gas is 1/7000 m³/Nm³. Initial concentrations of NO and NO₂ are 585 and 65 ppm respectively. total-N denotes the total amount of nitrogen in the gas phase.

Two properties, which are critical in the investigated system, are pressure and mass transfer conditions. The pressure controls the reaction rate of the NO oxidation and, thereby, the absorption rate of NOₓ and SOₓ, while the mass transfer limits transportation of species between the gas and the liquid phase. The mass transfer depends on the mass transport coefficient (kG) and the liquid surface area (a), which are both system dependent. Therefore, the importance of mass transport is evaluated by means of the product kGa. In Figure 2, the normalized NOₓ emission (NOₓ/NOₓ, initial) is calculated for a pressure range of 1 to 30 bar and for kGa values ranging from 0.25 to 4 times the
The $k_{Ga}$ value of the reference case ($k_{Ga0}$). The remaining parameter settings are kept the same as in the reference case. Three residence times are investigated: 25, 100, and 600 (not shown) seconds. The absorption is never complete because of the N₂O formation and the lowest NOₕ concentration in the gas phase is 78 ppm. For residence times longer than 600 seconds and pressures above 5 bar, the absorption is independent of both pressure (reaction rate) and mass transfer limitations. At a residence time of 100 seconds (Figure 2b) both mass transfer and pressure influence the absorption. However, when $k_Ga = k_{Ga0}$ and the pressure is above 20 bar the absorption approaches its maximum. As the residence time decreases, the importance of both the reaction rate and the transport rate increases and at 25 seconds (Figure 2a) both mass transfer and pressure strongly influence the absorption throughout the entire investigated range of pressure and mass transfer conditions.

Another important parameter is the amount of water added to the flue gas treatment. Figure 3 shows the percentage of SO₂ and NOₓ removal after 100 seconds at 20 bar as a function of the water to gas ratio. The upper water content corresponds to 98% sulphur removal and the lower limit corresponds to pure flue gas condensation (i.e. no added water). The SO₂ absorption is improved significantly by the addition of relatively limited amounts of water; absorption of 90% of the SO₂ requires around 0.1 m³ of water per m³ of flue gas. However, to further increase the absorption, large amounts of water is required; 98% absorption of the SO₂ requires more than 0.3 m³ of water per m³ of flue gas. The absorption of NOₓ is more complex. Initially, the absorption is enhanced by additional water. However, the NOₓ absorption is decreased by the reaction between HNO₂ and H₂SO₃, which forms N₂O. For low liquid fractions, the low absorption rate allows NO to be oxidized in the gas phase forming an NO₂ rich atmosphere, which results in a higher HNO₃ formation per dissolved NO and NO₂ molecule. As the liquid content is increased, more NO is absorbed via HNO₃ and, consequently, more N₂O is formed. At even larger amounts of added water, the absorption is increased, as the dissolved species become diluted and the absorption becomes more dependent on the solubility than on the reaction rates. The negative effects of water addition on NOₓ absorption is not seen for a sulphur free system where the absorption of NOₓ is favoured by an increasing water content.

Figure 2. Normalized emission of NOₓ (NOₓ/NOₓ, initial) at pressures from 1 to 30 bar and at $k_{Ga}$ from 0.25 to 4 times the mass transfer coefficients of the reference case ($k_{Ga0}$) after a) 25 seconds and b) 100 seconds.

Figure 3. SO₂ and NOₓ removal after 100 seconds at 20 bar as a function of water to gas ratio.